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# Island formation and manipulation of prochiral azobenzene derivatives on Au(111)

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## Abstract

Based on previous work with very similar azobenzene derivatives, this study of *para*-TBA (2,2′,5,5′-tetra-*tert*-butylazobenzene) molecules aims to identify single intact molecules and investigate their adsorption behavior on a Au(111) surface. The molecules are found to be mobile on the surface at the deposition temperature, leading to highly ordered and enantiomerically pure molecular islands. Voltage pulses between the surface and the tip of a scanning tunneling microscope are used to change the chirality of the adsorbate molecules. On the Cu(111) surface instead, single molecules are found on the terraces, which points to a stronger molecule–substrate interaction.

Molecular switches are molecules that exhibit at least two stable states, associated with characteristic physicochemical properties, which can be achieved reversibly by an external stimulus [1]. Such molecules are of great importance in nature, a well-known example is the retinal molecule, which is key for the process of vision in humans and animals [2]. In addition, they are very promising for future applications in molecular nanotechnology, where a specific physical or chemical property—for instance their conductance [3, 4]—can be changed in a controlled way in a nano-circuit or sensor arrangement. While molecular switches have already been studied in solution [5, 6], only little has been known until recently about their adsorption on a surface. Such a configuration is however very interesting, because it allows one to investigate the intermolecular interactions and self-organization in a two-dimensional confinement, which is also desirable for potential device applications. From a fundamental perspective, the role of a well-defined crystal surface in the vicinity of the molecule, and the coupling between them can be investigated. Based on these ideas, various studies have been carried out over recent years investigating molecular switches on surfaces, many of them on azobenzene, which consists of two benzene rings linked by a N=N azo linker, and its derivatives. It exists in two isomers, the planar *trans* and the three-dimensional *cis* form [7]. This molecule can be switched via light absorption in both directions (*trans* to *cis* and *cis* to *trans*) at different characteristic wavelengths by photo-isomerization [5]. Furthermore, thermal relaxation from *cis* to *trans* can be achieved as the *trans* isomer is energetically favored and after heating at elevated temperatures all molecules are found in the *trans* configuration [8]. Azobenzene derivatives have been intensely studied in recent years, both by local scanning tunneling microscopy (STM) [9–14] as well as by averaging spectroscopy techniques [8, 15, 16], and it turns out that side groups attached to the molecular core play an important role. On the one hand, they lift the molecule up from the metallic surface, which has been claimed to be important for the decoupling and thus the isomerization process [12]. However, more recent studies have shown that this lifting occurs mainly at the periphery of the molecule, but much less at the azo group in the center of the molecule, which is relevant for the isomerization [17]. On the other hand, chemical side groups can substantially change the isomerization behavior, resulting in a strong dependence on the atomic-scale environment and a spatial periodicity in the process that leads to characteristic switching patterns [18]. By exchanging the azo with a C=N

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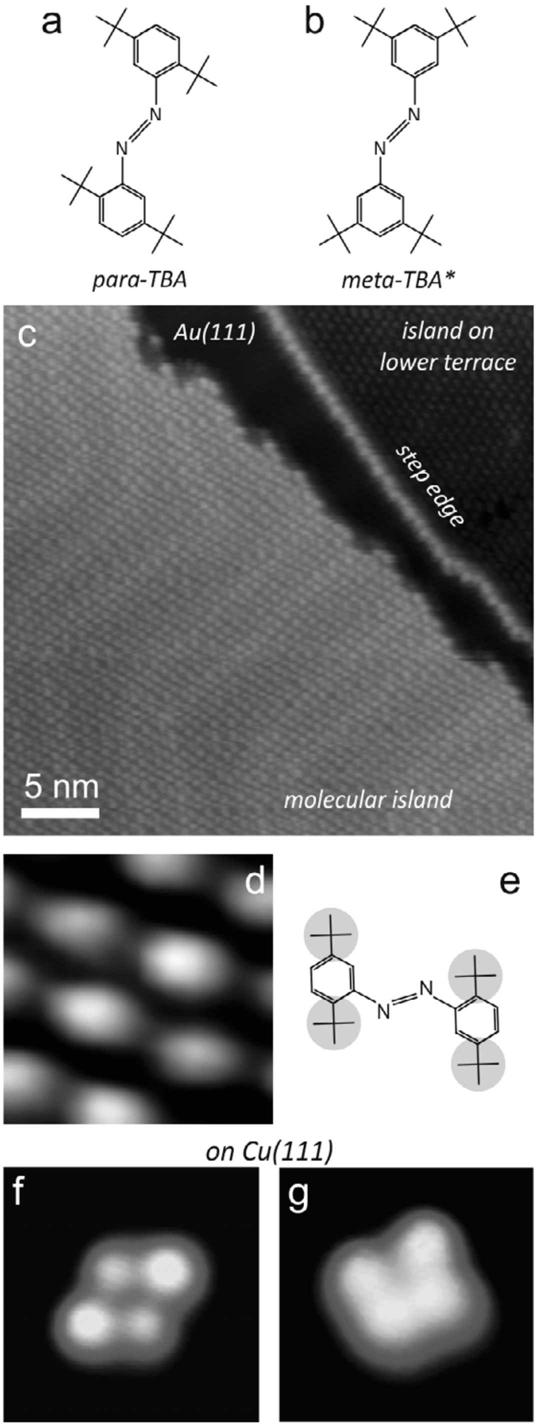

**Figure 1.** Chemical structures of the (a) *para*-TBA (2,2′,5,5′-tetra-*tert*-butyl-azobenzene; studied in this work) and the (b) meta-TBA (* studied previously [9, 10]) molecules. (c) STM image of a large surface area after deposition on Au(111), showing highly ordered molecular islands. (d) STM image of a smaller area with only one molecule and (e) the corresponding chemical structure (the *tert*-butyl groups that give rise to the protrusions in the STM images are marked by gray circles). (f), (g) STM images (both 2.5 × 2.5 nm$^2$) of the same molecules on a Cu(111) surface, representing two different adsorption geometries (see text).

group, and thus moving to imine derivatives, a quite different isomerization behavior was observed [19]. Note that the concept of *trans*–*cis* isomerization has recently been applied to molecular machines that are driven by such a chemical process [20, 21].

Here, we have studied azobenzene derivatives that are very similar to the previously studied [9, 10, 15] *meta*-TBA (3,3′,5,5′-tetra-*tert*-butylazobenzene) species, only exhibiting two of their four *tert*-butyl side groups at slightly different positions of the benzene rings. While for the previously investigated *meta*-TBA the *tert*-butyl groups are attached in 3- and 5-positions as well as 3′- and 5′-positions, in the case of *para*-TBA (2,2′,5,5′-tetra-*tert*-butylazobenzene) they are located in the 2- and 5-positions as well as 2′- and 5′-positions, i.e. in a *para*-relationship to each other (figure 1(a)). The consequence of this placement is twofold: on the one hand, the symmetry is reduced, leading to two different conformations for the *trans* configuration, i.e. a rhombic and a trapezoidal form, when rotating one benzene ring around the C–N bond axis. On the other hand, in *para*-TBA, one *tert*-butyl group per benzene ring is adjacent to the central azo connection, giving rise to steric repulsion and hence potential deviation from planarity.

The molecular adsorption on a gold surface is studied by STM, which is also able to induce molecular switching at the level of single molecules [22] and to correlate molecular processes with the atomic-scale environment of a single molecule [23]. Experiments were done in an ultrahigh vacuum chamber (base pressure around $10^{-10}$ mbar). Au(111) has been chosen as substrate, because it turned out to be sufficiently inert to allow molecular switching [9, 15], which is not the case on other noble metal surfaces or other reconstructions of the gold surface [10]. After cleaning the gold sample by conventional sputtering and annealing (at 800 K) sequences, the molecules were deposited from a Knudsen cell. In order to facilitate island formation of the molecules, the surface was kept at about 60 °C during deposition. Scanning tunneling microscopy (STM) images were taken with a home-built instrument [24] at a sample temperature of 7 K by applying a bias voltage to the sample. Typical scanning parameters are 0.1 nA tunneling current and bias voltages between 0.5 and 1.0 V.

When imaging the molecules on the surface (figure 1(c)), it is found that they form large close-packed islands after deposition, proving their mobility at the chosen sample temperature during preparation. The characteristic herringbone reconstruction of the Au(111) surface is still visible underneath the highly ordered molecular islands (figure 1(c)), showing that the substrate reconstruction is not influenced by the molecular adsorption. The step edges are covered by molecules, because they represent preferred adsorption sites due to their low coordination, and thus appear as bright stripes in the STM images (figure 1(c)). Individual molecules exhibit a very characteristic appearance, consisting of four lobes that can (in analogy to previous studies [9]) be assigned to the rather bulky *tert*-butyl side groups of the molecules (figures 1(d) and (e)). The exact precise identification of the molecules within a large island can be done by starting the assignment at the edges and then moving towards the center.

By measuring the lateral distance between intensity maxima of these lobes for many molecules in the STM

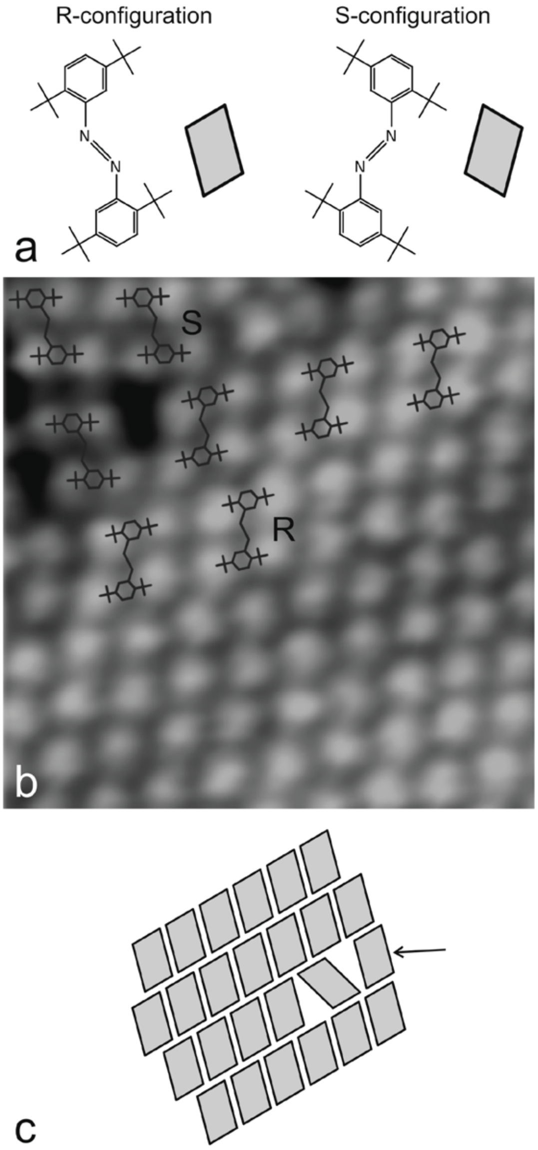

**Figure 2.** (a) Two enantiomers of the *para*-TBA molecules. Their rhombic appearance in the STM images, due to the *tert*-butyl groups, can be considered a rectangle that is either distorted to the right (R- configuration) or to the left (S- configuration). (b) STM image of a *para*-TBA island on Au(111) with both enantiomers visible as indicated. (c) Sketch of an enantiomerically pure island with a single defect from the other enantiomer.

images, we find approximately 6.2 and 6.9 Å as side lengths of the rhombic shape. This is in good agreement with the gas phase dimensions of the molecules of 5.9 and 6.3 Å (as calculated from molecular mechanics with the HyperChem 7 software), considering that the maxima of the apparent height are not necessarily positioned at the centers of the *tert*-butyl groups. The shorter distance is between *tert*-butyl groups at the same benzene ring, while the longer one is between *tert*-butyl groups at opposite benzene rings (see figure 1(a)). In addition to the rhombic shape of the molecules, these values show that the molecules are adsorbed in a planar geometry as *trans* isomers on the surface. This observation is not surprising, because the molecules are in the same state in the evaporator and can thermally relax during sublimation, and agrees with previous studies of azobenzene derivatives on surfaces [9, 15, 18]. Note however that—in contrast to the meta-TBA molecules—two of the four lobes appear slightly higher (by about 0.2 Å) than the other two, which is presented in figure 1(d) with a higher contrast. This height difference is not a result of the surface herringbone reconstruction, because it is observed for molecules that are fully adsorbed on the flat fcc areas of the Au(111) surface. It cannot be easily explained, but points to a slight rotation of the benzene rings from the planar geometry, most likely caused by steric repulsion imposed by the 2- and 2′-positioned *tert*-butyl groups located *ortho* to the azo linkage.

These results are compared in figures 1(f) and (g) with adsorption of the same molecules on the more reactive Cu(111) surface. This leads to a stronger molecule–surface interaction, which causes not only adsorption of single molecules on terraces (as in the images), but also the appearance of two shapes: rhombic and trapezoidal. In contrast to the Au(111) surface, the trapezoidal shape (8% of the molecules) is stabilized here in addition to the rhombic one (92%). This observation points to a molecular relaxation to the rhombic configuration after adsorption from the gas phase in the trapezoidal shape at room temperature on the gold surface. The molecular dimensions (5.2 and 5.7 Å) of the rhombus are slightly smaller than on the gold surface, probably due to the modified molecule–surface interaction. They are in agreement with the gas phase values (see above) and also here exhibit an asymmetry that leads to two enantiomers. Note that the *tert*-butyl legs exhibit different apparent heights also on this flat fcc surface, which confirms that they are not due to the herringbone reconstruction on Au(111). However, their intensity distribution changes between Au(111) and Cu(111), probably due to the different molecule–surface interactions.

Chirality is a unique property of molecules possessing elements of asymmetry, leading to the existence of pairs of enantiomers that exhibit different properties when interacting with other (pro)chiral molecules, and is hence of great importance in fields ranging from chiral sensing to separation and catalysis [25]. Thus, it is of great interest to produce enantiomerically pure compounds in contrast to racemic mixtures that contain both enantiomers of opposing chiralities in the same quantity [26]. As STM is very useful to locally probe the self-organization of chiral molecules, they have been studied intensely on surfaces in recent years [26–29]. While the *para*-TBA molecules in the present study exhibit no chirality in the gas phase, they are prochiral and can adopt either one of two enantiomeric forms after adsorption, i.e. they become chiral in the two-dimensional confinement of the surface [26]. Figure 2(a) shows the two enantiomers in the R- and S-configuration with a schematic rhombus that indicates their resulting overall shape, determined by the *tert*-butyl groups, in STM images. Both enantiomers are found in our STM images on Au(111), but it is important to note that each individual island is almost exclusively composed of only one enantiomer, thus being enantiomerically pure. The reason is attributed to the closer packing in a homo-chiral island, whereas the mixing of different enantiomers in the

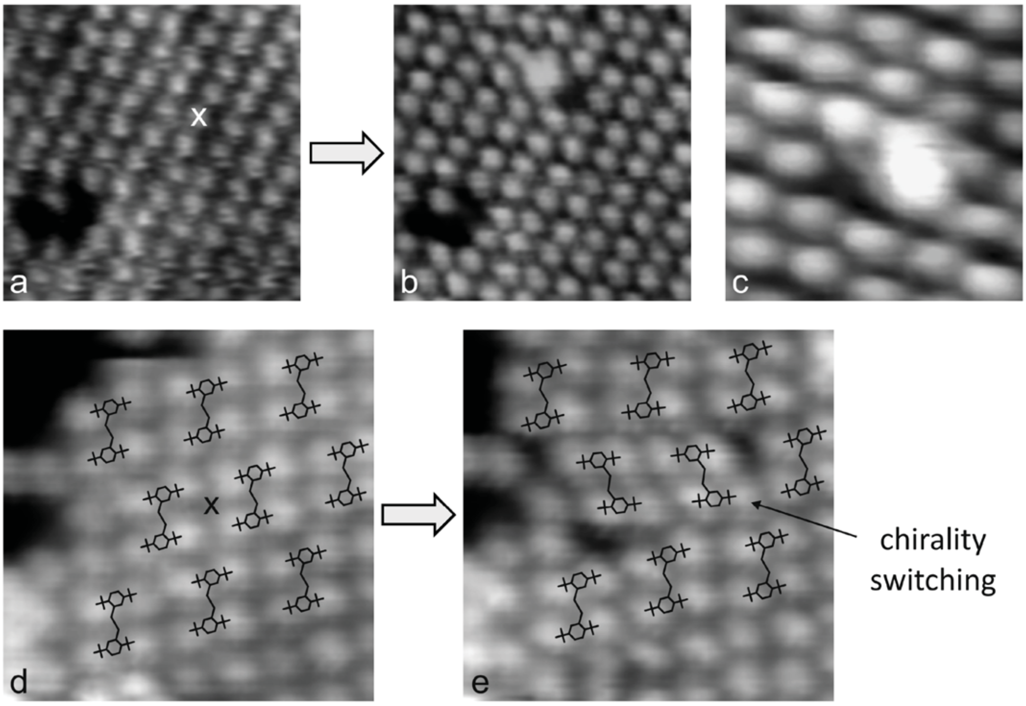

**Figure 3.** Manipulation by applying voltage pulses to *para*-TBA islands on Au(111) (the crosses indicate the tip positions). (a), (b) STM images on Au(111) (both $6.3 \times 6.3$ nm$^2$) of the same surface area as illustrated by the defect at the lower left corner before and after a voltage pulse (see text). (c) STM image ($1.6 \times 1.6$ nm$^2$) of a single molecule after a similar voltage pulse. (d), (e) STM images of the same surface area before and after a voltage pulse that leads to chirality switching (see text).

same island leads to a lower molecular density and weaker intermolecular interaction, thus an energetically less favored arrangement. Such a molecular packing is however found in some rare cases in the STM images. An example is presented in figure 2(b), with an island that consists of molecules in the R-configuration and some S-enantiomers at the edge. Such an arrangement at the border of an island is typical because the other enantiomer represents a defect in the island structure and further growth is unfavorable. This is visible in the sketch of figure 2(c), where a single molecule in S-configuration is located in an enantiomerically (R) pure island. First, holes in the island structure open and thus avoid closer packing and energy minimization, and second, island growth is stopped there because attached molecules (as the one marked by an arrow) do not attach in the same coordination symmetry as the other molecules of the highly ordered areas.

When attempting isomerization of the molecules by applying voltage pulses with the STM tip over a molecular island (similar to previous studies [9, 18]), bias voltages between 1 and 3.5 V and tunneling currents of up to 50 nA were used. In some cases (about 70 examples in more than 800 attempts), changes in single molecules were observed when using bias voltages of about 2.2 V. They all led to similar changes, with a typical example in figures 3(a) and (b), where a molecule appears as a bright lobe after the voltage pulse. From an analysis of the surrounding molecules, it becomes clear that this feature is related to a single molecule (figure 3(c)). Note that *cis* isomers of the *meta*-TBA molecules appeared as protrusions after switching them from the *trans* to the *cis* state [9], indicating that an isomerization process from *trans* to *cis* might have taken place. Alternative explanations are the dissociation of molecules, which seems unlikely as such a process typically occurs at higher bias voltages, and contamination from the tip that would not be as stable in subsequent scanning. However, we cannot completely exclude these two effects from our experiments. An important observation is that switching of the molecules back to the initial state could never be induced. Hence, no reversibility could be observed and there is no clear proof for a molecular isomerization. These results show that a small variation of the molecules (from *meta*-TBA to *para*-TBA) leads to a substantial change in the isomerization behavior, being either irreversible or not achievable with comparable STM manipulation parameters.

Although it is not clear whether isomerization really takes place, another change in the molecules could be observed rarely after STM pulses (using similar bias voltages and pulse lengths) as molecules change their chirality. Figures 3(d) and (e) show such an example, where a close-packed island is imaged and the molecular configuration is assigned (as indicated by the superimposed structures), revealing that the observed area is enantiomerically pure (R-configuration) before the voltage pulse. After taking the STM image, a voltage pulse was applied (at the position of the cross, shown in figure 3(a)), ramping the voltage from −2.2 to +2.2 V (to cover a wide range of electron energies) at a fixed tip height above the sample over a period of 180 s. Interestingly, the chirality of two molecules in the island—close to the tip position during the voltage pulse—was changed in this manipulation as they adapt the other enantiomers

(S-configuration). Consequently to this switching of the chirality, two holes appear (similar to the sketch in figure 2(c)) and some molecules rearrange in the vicinity of the tip position during the pulse.

As the molecules are chiral in the two-dimensional confinement of the surface, a simple rotation in the plane of the surface cannot change chirality. Instead, there are two other ways in which such a chirality change could be explained. Either the molecule is completely lifted from the surface and re-adsorbs on its opposite face or the modification occurs in two separate steps (which can occur in either order with an intermediate configuration that is sterically less favorable than the initial and final rhombic shape): (1) rotation of one benzene ring around the adjacent C–N axis and (2) the rotation of the other benzene ring together with the azo group around the same C–N axis. The latter sequential option seems more likely, because on the one hand the energy barrier is smaller than for a complete lifting. In addition, a similar process has been reported recently by Linderoth and co-workers, who observed a thermally induced rotation of a benzene ring in planar adsorption with various side groups, there also leading to a switching of the molecular chirality [29]. Although the rotation of only one benzene ring in the *para*-TBA molecules should be easily distinguishable in the STM images by the trapezoidal shape of the intermediate conformation, it has not been observed in our experiments. This is likely due to steric hindrance of the *tert*-butyl groups; two of them would get very close to each other in such a trapezoidal intermediate and hence only pairwise rotation of the molecules from one enantiomer to the opposite enantiomer is observed. Note that while the possible isomerization process (figures 3(a)–(c)) can take place anywhere in a molecular island, the chirality switching of *para*-TBA molecules occurs only at island borders or close to vacancies (as in figures 3(d) and (e)). This is in agreement with the additionally required area for a racemic mixture from a simple geometric consideration (see figure 2(c)). Such extra space cannot be created in the center of an enantiomerically pure close-packed island, where the dislocation of many molecules would be needed.

Note that in contrast to the Au(111) surface, manipulation experiments with the same *para*-TBA molecules on the Cu(111) do not lead to switching processes, but only to many different molecular appearances after the voltage pulse that most likely reflect dissociation processes. The lacking isomerization on the Cu(111) surface is in agreement with previous results for meta-TBA [10] and is thus not unexpected. The absence of chirality switching on the other hand is probably due to the stronger molecule–surface interaction, which causes a higher barrier for such a substantial change of the adsorption configuration.

In conclusion, we have studied the adsorption of *para*-TBA molecules on a Au(111) surface and find highly ordered islands due to the molecular mobility during adsorption. Single molecules are identified and exhibit a very characteristic appearance, revealing that only *trans* isomers are present on the surface. Furthermore, these molecules are found to be prochiral, and enantiomerically pure islands with ‘chiral defects’ mainly at the edges are observed. Manipulation experiments indicate isomerization processes, even though a clear proof—in particular reversibility—is missing. Furthermore, chirality switching is observed where single molecules change from one enantiomer to the other, probably by a twofold internal rotation.

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